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# DETERMINATION OF HEXAZINONE RESIDUES AND THEIR FATE IN A NEW BRUNSWICK FOREST

by

J. FENG and C. FENG

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## ABSTRACT

A clearcut site near St. Leonard, New Brunswick was treated with hexazinone, 3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione, at nominal rates, 3.1 and 3.8 kg ai/ha by a fixed wing aircraft equipped with a conventional boom and nozzles. On-target deposit at soil plots was highly variable, averaging 2.53 kg/ha with 37% CV. Off-target deposit monitored with 400 $cm^2$ deposit plates decreased rapidly to 0.006 kg/ha at 70 and 100 m downwind. In spiked soil trials, recovery varied with concentration and residue, with means ranging from 91.5 - 98.3%, 62.9 - 88.6% and 101.4 - 104.2% for hexazinone and its metabolites A, 3-(4-hydroxycyclohexyl)-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione and B, 3-cyclohexyl-6-(methylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione, respectively. Hexazinone recovery in fresh and air-dried samples of spiked humus soils was 114 and 110%, respectively. A consistency of 6.9% CV for hexazinone subsampling, extraction and analysis was determined from 50 homogenized air-dried soils. Log-log hexazinone residue disappearance relationships with time (up to 537 days after application) were found with correlation coefficients of the means ranging from $r = 0.88$ to 0.98, with 50% of the initial residues calculated to remain after 8, 28 and 13 days for upper (0-15 cm), lower (15-30 cm) and their combined (0-30 cm) soil layers, respectively; and with 10% to remain after 49, 319 and 122 days, respectively. Hexazinone leaching to the lower soil layer was dependent on rainfall, and peaked at 0.6 kg/ha (0.46 µg/g) after 6 days when cumulative rainfall reached 29 mm. Residue value reporting formats µg/g, and kg/ha were compared. Soil residues monitored at various distances off-target were correlated to off-target deposit rates as determined by analyses of deposit collector residues. Lateral residue movement at stations 10 and 20 m downslope (5%) was found from 6 to 61 days after application. Lateral residue movement to 50 m downslope was found in the first two weeks. No residues were found at 100 m downslope throughout the 537-day monitoring period. Hexazinone residues were detected in streamwater throughout the 45-day period when runoff in 6 storm events was monitored. Residues decreased both with time after application and with distance downstream. The initial peak concentration at 50 m downstream was 30.8 ppb during the first storm event 6 days after application, and decreased rapidly to 3.7 ppb after 45 days; concentration at 800 m downstream was 5.1 ppb during the second storm event 13 days after application and decreased to less than 1 ppb between 20 and 45 days after application. No residues were found at 1500 m downstream throughout the monitoring period.

## RÉSUMÉ

Un terrain de coupe rase près de Saint-Léonard (Nouveau-Brunswick) a été traité à l'hexazinone (3-cyclohexyl-6-(diméthylamino)-1-méthyl-1, 3,5-triazine-2,4(1H,3H)-dione) à des taux nominaux, soit de 3,1 et de 3,8 kg/ha d'ingrédients actifs, à l'aide d'un aéronef à voilure fixe équipé d'une rampe de pulvérisation ordinaire. Le dépôt sur les lots-cibles était fortement variable, étant en moyenne de 2,53 kg/ha avec un C.V. de 37 %. Les dépôts à l'extérieur de la zone-cible, évalués à l'aide de plaques à dépôts de 400 $cm^2$, ont diminué rapidement à 0,006 kg/ha à 70 et 100 m en aval par rapport au vent. Lors d'essais de sol enrichi, le taux de récupération variait selon la concentration et les résidus, avec des moyennes comprises entre 91,5 et 98,3 %, 62,9 et 88,6 % et 101,4 et 104,2 % pour l'hexazinone et ses métabolites, soit la 3-(4-hydroxycyclohexyl)-6-(diméthylamino)-1-méthyl-1, 3,5-triazine-2,4(1H,3H)-dione et la 3-cyclohexyl-6-(méthylamino)-1-méthyl-1,3,5-triazine-2,4(1H, 3H)-dione, respectivement. Le taux de récupération d'hexazinone dans des échantillons frais et séchés à l'air d'humus enrichi était de 114 et de 110 %, respectivement. À partir de 50 échantillons homogénéisés séchés à l'air, on a calculé un C.V. constant de 6,9 % pour la préparation de sous-échantillons, l'extraction et l'analyse de l'hexazinone. Les courbes log-log de la disparition des résidus d'hexazinone en fonction du temps (jusqu'a 537 jours après l'application) correspondaient à des coefficients de corrélation de moyennes comprises entre r = 0,88 et 0,98 ,50% des résidus initiaux calculés persistant après 8, 28 et 13 jours dans le cas des couches supérieures (0-15 cm), inférieures (15-30 cm) et combinées (0-30 cm), respectivement, et 10 % restant après 49, 319 et 122 jours, respectivement. La lixiviation de l'hexazinone vers les couches inférieures du sol dépendait de la pluie et atteignait 0,6 kg/ha (0.6 µg/g) après 6 jours, quand la valeur cumulative des précipitations de pluie atteignait 29 mm. On a comparé les types de mesures de valeurs des résidus, soit en µg/g et en kg/ha. Les résidus de sol surveillés à diverses distances au-delà de la cible ont été correlés avec les taux de dépôt à l'extérieur de la cible, mesurés selon des analyses des résidus de dépôts. Le déplacement latéral des résidus à des stations à 10 et à 20 m suivant une pente négative (5 %) a été mesuré entre 6 et 61 jours après l'application. Le mouvement latéral des résidus à 50 m suivant une pente négative a été mesuré au cours des deux premières semaines. On n'a observé aucun résidu à 100 m suivant une pente négative au cours de toute la période de surveillance de 537 jours. On a décelé la présence de résidus d'hexazinone dans les cours d'eau pendant toute la période de 45 jours au cours de laquelle on a surveillé les eaux de ruissellement de 6 orages. Les résidus diminuaient en fonction du temps après l'applicatin et de la distance en aval. La concentration de pointe initiale à 50 m en aval était de 30,8 pp $10^9$ au cours du premier orage, 6 jours après l'application, et a diminué rapidement à 3,7 pp $10^9$ après 45 jours; la concentration à 800 m en aval était de 5,1 pp $10^9$ au cours du deuxième orage, 13 jours après l'application, et a diminué à moins de 1 pp $10^9$ entre 20 et 45 jours après l'application. Aucun résidu n'a été observé à 1500 m en aval pendant toute la période de surveillance.

## INTRODUCTION

Hexazinone has had temporary registration for forestry use in Canada since 1984. Its use is currently restricted to ground applications only for both site preparation and conifer release (Reynolds et al. 1986). Data on the behavior of hexazinone in the Canadian forest environment are required before it can be considered for full registration for forestry use.

The validity of laboratory-generated models in predicting herbicide movement and fate in ecosystems requires verification with systematic field evaluation (Neary et al. 1983). The persistence and mobility of hexazinone in soils was found to be dependent on soil type and climate. Field soil studies reported in the USA and elsewhere indicated that hexazinone has a half-life of between 1 and 6 months (Rhodes 1980; WSSA 1983), and the potential for off-site movement of at least 2 m down a 12-22 degree slope (Barring and Torstensson 1983; Harrington et al. 1982). Herbicide movement in water from application with a pelleted form of hexazinone (Velpar Gridball ) has also been studied: in a stream oversprayed by hexazinone pellets, water-borne hexazinone decreased to less than half of the initial concentration within one hour of application at a point adjacent to the treated area (Miller and Bace 1980). When stormflow and baseflow were monitored through 26 storm events in a 13-month period, 0.53% of the hexazinone applied was calculated as lost through runoff (Neary et al. 1983). And in another study, no residues were found in groundwater or springflow beyond 20 m from the treated area (Neary 1983). However, the behavior of hexazinone in the Canadian forest environment, has not been systematically evaluated.

The specific objectives of this study were to:

1) determine hexazinone deposit on the forest floor and its persistence and leachability in New Brunswick loam soils;

2) determine the off-site mobility of hexazinone in soil on a slope;

3) monitor the off-site movement of hexazinone in snowmelt, baseflow and stormflow;

4) measure off-target deposit from aerial application;

5) measure the occurrence and disappearance of two primary metabolites A and B;

6) establish a new reporting method for hexazinone residues in soil on an area (kg/ha) basis to provide direct comparison with the rate of application.

## MATERIALS AND METHODS

### *Site Description*

Two 3.7 ha plots clearcut in 1980-81, were located on J.D. Irving property near St. Leonard, in the northwest corner of New Brunswick. Prior to herbicide treatment, the few scattered residual snags (10-20 m tall) were felled to allow accurate aerial application. The dominant weed species was raspberry *[Rubus idaeus* L. var strigosus (Michx.) Maxim.]. Other brush species included pin cherry *(Prunus pensylvanica* L.f.), striped maple *(Acer pensylvanicum* L.), mountain maple *(A. spicatum* Lam.), red maple *(A. rubrum* L.), and sugar maple *(A. saccharum* Marsh.). The intended crop species for planting was white spruce *[Picea glauca* (Moench) Voss]. Naturally regenerated balsam fir *(Abies balsamea* (L.) Mill] was also observed on the site.

The experimental site was located within two drainage systems and was generally flat. It was subdivided into two spray blocks (Fig. 1). Spray Block No. 1 drained to the west directly into Big Brook River. The surface gradient was 5% for the first 150 m west of Block No. 1 and before the clearcut boundary, then 10-20% for the remaining 350 m of uncut buffer to the river. Vegetation averaged less than 0.5 m

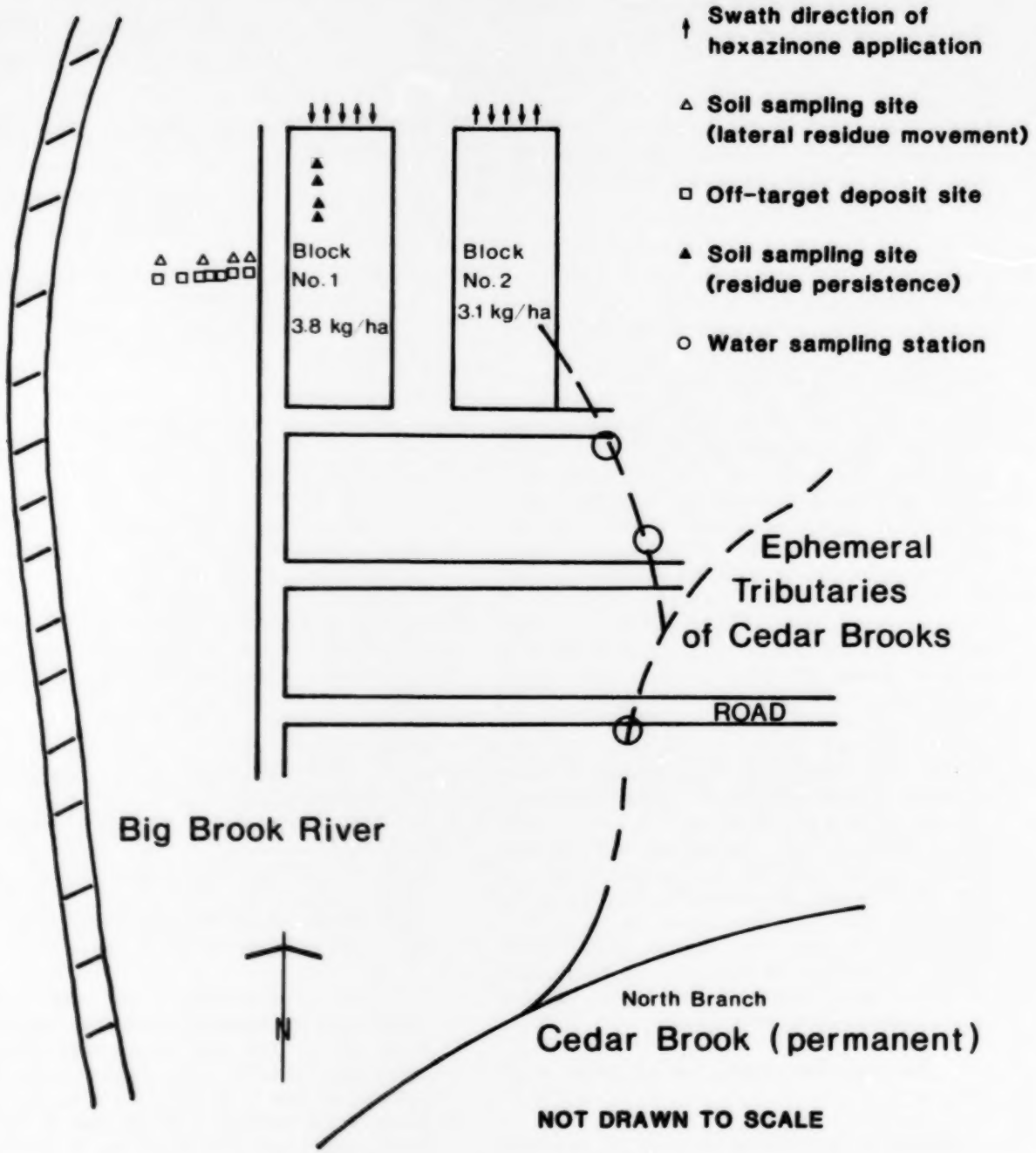


Figure 1. Study site locations near St. Leonard, New Brunswick.

in height in the clearcut area and a uniform 15 m in the uncut area. Off-target deposit stations and lateral-residue-movement-plots were located on the 5% portion of the slope (Fig. 1) on an old logging track about 10 m wide and 1 m below ground level, perpendicular to the middle of the western edge of block No. 1. Off-target deposit stations were at distances of 5, 10, 20, 30, 40, 50, 75 and 100 m downwind, and soil plots for lateral residue movement studies were at 10, 20, 50 and 100 m downslope. Four soil plots for monitoring herbicide residue persistence and leaching were located in spray block No. 1. The plots were located in the first spray swath, in the upper portion of the spray block, about 50 m apart. There was no overland flow from snowmelt at the time of herbicide application.

Spray block No. 2 drained to Cedar Brook through ephemeral stream channels that flowed only during snowmelt and spring storm events (Fig. 1). Water sampling stations were established along these stream channels at 50, 800 and 1500 m downstream from the southeastern corner of block No. 2 to monitor herbicide runoff. The 50 m station collected snowmelt runoff from block No. 2, observed at the time of herbicide application. Water samples from the 800 m station were collected from a 20 cm deep pool (0.5 m diameter), and those from the 50 and 1500 m stations were sampled on the downstream (south) side of road culverts. The loam soils of this area contained about 4% organic matter and had a pH of 5.2.

*Herbicide Application*

The two spray blocks (84 x 445 m each, separated by a 50 m buffer, Fig. 1) were treated on 19 May 1984 with hexazinone (Velpar L at 240 g ai/L) at 3.8 kg ai/ha and 3.1 kg ai/ha for blocks No. 1 and 2, respectively using a Turbo Thrush Commander equipped with an Airfoil boom with 66 Whirljet 1/8 B-10 No. 3 conetip nozzles (32 +tips, 34 -tips) set at 180 degrees. The aircraft flew 193 km/h at an 18 m elevation.

Application was completed with 5 longitudinal swaths per plot (Fig. 1). Flags were used for marking the location of individual swaths.

The sky was clear at the time of application. There were 2 mm of rain two days before and 2 days after, and 27 mm of rain 5 days after treatment. An east wind (3-5 km/h) blew during treatment of block No. 1, and a west wind of the same speed during treatment of block No. 2. Relative humidity (64%) and air temperature (15°C) were recorded at a field weather station during application .

*On- and Off-Target Deposit*

Construction and installation of deposit collectors were similar to that reported by Feng and Klassen (1986). The deposit plates were placed 10 cm above the ground in clearings surrounded by a few scattered pieces of slash, and shrub vegetation bare of foliage and less than 1 m in height. Eight main off-target drift deposit stations were located west of treatment block No. 1 with five supplementary stations in the east as described above. Sixteen on-target deposit stations were at the locations of 4 soil plots, with collectors on the 4 sides of each plot. One station was in line with an off-target deposit station.

Deposit samples were packaged about 30 min after herbicide application when the collection surfaces were dry. Clean vinyl disposable gloves and forceps were used for removing the tape from the aluminum foil collection surfaces. Care was taken so that no contaminated articles contacted the aluminum foil sheets. The upper sample sheets were folded and then wrapped with the lower sheets before being placed in labelled plastic bags (25 x 40 cm) (Feng and Klassen 1986). Samples were cooled in an ice chest immediately after collection. Temperatures were maintained near 0°C during shipment from the field freezers (-5°C) to the analytical lab in Sault Ste.

Marie, Ontario using insulated commercial coolers and a covering of frozen cooler packs.

*Soil Sampling*

Preparations for soil sampling included removal of slash and large debris from the soil plots. Vegetation was trimmed down to about 1 cm above the ground inside and to 0.5 m outside each plot to allow full herbicide deposition on the ground to generate a worst case scenario. Disturbance to the forest floor was kept to a minimum.

One soil core was collected at each of the 4 residue persistence plots (16 $m^2$) and the 4 lateral residue movement sites 1 day before and 1 hour, 3, 6, 13 days, 1, 2, 3, 4, 5, 6, 12, 18 months after treatment. Soil cores were taken with a Campbell soil auger (9.2 cm diameter) (Feng and Klassen 1986), and divided into subsamples, separating soils 0-15 cm from soils 15-30 below the surface. Samples were immediately cooled and kept in ice-filled coolers (Coleman) after collection and frozen (-5°C) within 8 hours. The temperature of the samples was maintained at about 0°C in commercial coolers during shipping to the analytical laboratory. The samples were maintained at -14°C at the analytical laboratory prior to analysis.

*Water Sampling*

Runoff water samples were collected at the three stations described above one day before treatment and with collection times selected to correspond with the major rain events immediately following treatment. Six storm events were monitored for hexazinone runoff during a 45-day period between May 25 and July 3, 1984. Water samples were collected at 3, 7 and 14 days after each storm event and before the start of the next storm event. Samples were taken by collecting approximately 900 mL in 1 L polypropylene bottles prewashed with methanol. Samples were cooled immediately in an ice-filled cooler and frozen (-5°C) within 2 hours of collection. Shipping to, and storage at, the analytical laboratory was similar to that for the soil and deposit samples.

*Sample Preparation*

Deposit Samples: Hexazinone residues on the deposit collectors were extracted from the aluminum foil with a procedure modified from methods of Feng and Klassen (1986) and Holt (1981). The aluminum foil was initially rinsed with 150 mL of extracting solution (acetone/water; 80:20; V/V) then cut into strips, sonicated (3 min) and shaken (3 min) on a reciprocating shaker with 3 x 150 mL extracting solution in a Teflon bottle. The rinse and washings were pooled and flash-evaporated in a rotary evaporator under reduced pressure at 60°C until only the aqueous phase (100 mL) remained. Residues were extracted by partitioning with 3 x 100 mL ethyl acetate, and passed through a 30 g anhydrous sodium sulfate column, which was pre-washed with ethyl acetate. The extracts were either concentrated using a vacuum rotary evaporator and an N-Evap (Organomation model III) or diluted with ethyl acetate to 10-2500 mL before gas chromatographic (GC) analysis.

Soil Samples: Soil core sections were prepared for extraction by weighing, air-drying (to 5% moisture content), homogenizing and sieving (2 mm mesh) the soils, as described by Feng and Klassen (1986). Total weights of fresh samples, air-dried samples and pebbles ( 2 mm diameter, which were contained in the samples and discarded later), were measured. Sample air dry weights were used to compute data from µg/g to area (kg/ha) and volumetric (mg/L) bases (Feng and Klassen 1986). The processed soils were also used to determine soil texture and chemical properties.

Hexazinone residues were extracted and purified based on Holt's (1981) method. Holt's method was modified to prevent fine clay particles from entering the filtrate before cleanup by liquid/liquid partition,

and formation of precipitates in the final concentrates during cold storage. The method was also simplified by avoiding chromatograhic column cleanups and derivatization by trifluoroacetic anhydride, which created unstable (8h) final products and a wide range of percent recovery (64-124% in soils). The modified method is briefly summarized as follows. An aliquot of 25 g processed air-dried soil was weighed in a 250 mL Nalgene bottle (Nalge 2107), wetted with 15 mL of distilled water, capped tightly and shaken horizontally for 15 minutes on an Eberbach reciprocating shaker at 280 excursions per minute. Sixty mL of acetone were then added. After being shaken for another 15 min, the sample was centrifuged at 350 x g (1150 rpm, rotor radius 23.8 cm) for 10 min. The extracts were filtered through a Millipore Filter Apparatus (47 mm) with Mitex disc filters (5 $\mu$m, Millipore LSWP 04700) under reduced pressure. Soils were extracted twice more, each with 75 mL of an acetone-water solution (80:20; v/v), 2 min of agitation and 10 min of centrifugation similar to that described above. The extracts were filtered through the same apparatus described above, combined with the first extract, and the acetone was flash-evaporated in a vacuum rotary evaporator at 60°C. The remaining aqueous solution was washed and extracted with 3 x 50 mL of n-hexane (discarded) and 3 x 75 mL of chloroform, respectively. Chloroform extracts were combined, passed through anhydrous sodium sulfate, and flash-evaporated to dryness. The residues were re-dissolved in 50 mL of acetonitrile and washed twice each with 50 mL of n-hexane. The acetonitrile phase was flash-evaporated to dryness. The residues were finally dissolved in 2-10 mL of ethyl acetate and filtered with Millex SR (0.5 $\mu$m) filter units (Millipore SLSR 025NB) before GC analysis. After preliminary analysis, if a concentrated sample extract contained more than twice the concentration of that in the mix-standard solution (see Gas Chromatography), the sample extract was diluted to near the concentration of the mix-standards and was reanalyzed (Feng 1987).

Water Samples: Water samples (500 mL) were extracted by serial liquid-liquid partitioning with ethyl acetate (3 x 200 mL). The amount of ethyl acetate used in partitioning was proportionally increased when larger volumes of water sample were to be extracted. The extracts were pooled and concentrated by using a vacuum rotary evaporator and an N-Evap to 2-10 mL before GC analysis.

*Gas Chromatography*

Purified sample concentrates in ethyl acetate were analyzed alternately with mix-standard solutions containing 2.5, 5.0 and 10.0 ppm of hexazinone and metabolites B and A, respectively, on a Varian VISTA 6000 GC equipped with a thermoionic specific detector (TSD) and a VISTA data system (DS402). The specific gas chromatographic conditions were as follows:

chromatographic column: 60 cm glass, 2 mm i.d., packed with 10% SP2250DA on 100/120 Supelcoport, and with Acid-treated glass-wool plugs;

temperatures: Injector - 260°C Detector - 300°C;

Column Temperature Program - 240°C (2.5 min) - 10°C/min - 280°C (3.5 min);

gas flow rates: N2 (Linde, UHP grade) - 33 mL/min; H2 (Linde, prepurified) - 4.5 mL/min; air (Linde, zero gas grade) - 175 mL/min.

Retention times under these GC conditions were 2.6, 3.5 and 5.5 minutes for hexazinone and its metabolites B and A, respectively. Peak heights were used for the calculation of residue concentration. When a sample injected showed more than 5 ppm of hexazinone, the sample was diluted to near 2.5 ppm with ethyl acetate, and re-analyzed (Feng 1987). The average of two corresponding peak heights (i.e., hexazinone) was obtained from a mix-standard solution analyzed immediately before and after sample

analysis. A 10% range about the average of pre- and post-standard values was used as the rejection threshold (Feng 1987).

## RESULTS AND DISCUSSION

### *On-Target Deposition*

Hexazinone deposit averaged 2.53 kg ai/ha at 16 stations monitored in the target area, equating to 66.3% of the planned application rate with a high variation of deposit values (37% CV or coefficient of variation) (Table 1). Variation was also high at collection stations clustered around soil plots, with averages (n=4) of 2.94 (40%CV), 2.21 (42% CV), 1.99 (45% CV) and 2.98 kg/ha (18% CV) for soil plots 1, 2, 3 and 4, respectively (Table 1). Hexazinone's metabolites A and B were not detected in any of the 16 samples, indicating that appropriate sample handling and storage techniques were followed.

Table 1. Hexazinone deposited at treated soil plots as indicated by plate deposit collectors (400 $cm^2$)

| Replication | Hexazinone (kg/ha) Plot 1 | Plot 2 | Plot 3 | Plot 4 | Total |
|---|---|---|---|---|---|
| 1 | 2.78 | 3.47 | 1.47 | 2.54 | |
| 2 | 4.65 | 1.52 | 1.72 | 2.55 | |
| 3 | 2.24 | 1.52 | 1.44 | 3.61 | |
| 4 | 2.11 | 2.34 | 3.33 | 3.23 | |
| Mean | 2.94 | 2.21 | 1.99 | 2.98 | 2.53 |
| CV | 40% | 42% | 45% | 18% | 37% |

### *Off-Target Deposit*

Wind direction at the time of application was from the east, conducive for monitoring off-target deposit on the western side of the spray block. Hexazinone deposition 10 m within the treated zone was 2.43 kg ai/ha, or 63.6% of the planned application rate. This deposition value was 4% lower than the average deposition from the same spray swath at the soil plots (2.53 kg/ha) about 80 m north. Off-target deposit decreased rapidly with distance, from 2.43 to 0.006 kg/ha at 10 m within and 100 m downwind of the treated zone, respectively (Table 2). Linear regression analysis indicated a log-log relationship for deposit and distance downwind, log Y = 2.47 - 2.33 (log X) for Y = hexazinone deposited (kg/ha) and X = distance downwind (m). Data values fit very closely to the linear regression, with a significant correlation coefficient (r) of -0.97. The coefficient of determination ($r^2$) indicated the regression equation accounted for 94% of the variation in data values. Extinction rates calculated from the regression equation indicated that 50, 10, 1 and 0.5% of full hexazinone deposition (2.43 kg/ha) would be expected at 10.6, 21.1, 56.7 and 76.2 m downwind, respectively, under the specific conditions of this study.

Table 2. Hexazinone deposit at downwind distances by aerial application with conventional boom and nozzles

| Downwind[a] Distance (m) | Hexazinone Residues Per Plate (µg)[b] | Calculated (kg/ha) |
|---|---|---|
| -10 | 9720 | 2.43 |
| 10 | 3410 | 0.85 |
| 20 | 1236 | 0.31 |
| 30 | 725 | 0.18 |
| 40 | 266 | 0.067 |
| 50 | 203 | 0.050 |
| 75 | 24.1 | 0.006 |
| 100 | 25.3 | 0.006 |

[a] Wind speed (3-5 km/h); relative humidity (64%); air temperature (15°C).

[b] Detection limit was 0.25 µg per plate.

*Recovery of Hexazinone in Soils*

In spiked soil trials, recovery varied with concentration and with residue analyzed. Percent recoveries of hexazinone and its metabolites A and B from soil spiked at 1, 4 and 2 µg/g were 98.3% (8.6% CV), 88.6% (15.4% CV) and 104.2% (8.7% CV), respectively. When the soil was spiked with lower hexazinone concentrations at 0.1, 0.4 and 0.2 µg/g, recoveries were 91.5% (7.8% CV), 62.9% (11.8% CV) and 101.4%, (13.0% CV), respectively. Subsequent soil residue values were adjusted for recovery by the appropriate recovery values.

*Hexazinone Recovery Through Air Drying*

Recovery of hexazinone from soil samples spiked prior to air drying was measured to determine whether degradation occurred during drying. Dao et al. (1982) found that air drying field samples did not modify soil properties nor the adsorption capacity of soils. When frozen samples were air dried in this study, the rapid loss of 70% of the total moisture content in the first day minimized the possibility of microbial degradation of hexazinone in the samples. Further drying yielded an average 3.8% moisture content from an initial average 31.3% found in fresh field samples.

Recovery of hexazinone through air-drying soil was measured in 500 g humus with a 56% moisture content. The humus was thoroughly blended before and after application of hexazinone by the Ontario Ministry of Natural Resources Lab in Maple, Ontario, at 0.5 kg ai/ha to a 5 cm layer. Samples were in transit for 2 days (0°C) as described by Feng and Klassen (1986), and held in cold storage (-14°C) for one month before being analyzed. One half of the sample (250µg) was air-dried for 3 days, then homogenized as described by Feng and Klassen (1986). Four aliquots each of wet (~5µg) and dried (15µg) soil samples were analyzed for hexazinone recovery. Bulk densities were measured for both wet and dried samples to enable values to be reported in different formats. Bulk density data permitted the conversion from traditional residue reporting on a weight basis (µg/g) to either a volumetric (µg/mL) or an area (kg/ha) basis. The latter reporting format allowed direct comparison between samples of different porosity or composition. Air drying trial recovery results were reported in all three bases (µg/g; µg/mL; kg/ha) to illustrate the benefits of the new reporting format. Results (Table 3) indicated that the air-drying procedure described by Feng and Klassen (1986) provided a residue value consistency (4% CV) superior to direct analysis of wet soils (33% CV). Results also indicated that there was no loss of hexazinone through air-drying (110% recovery) compared to the wet samples (114% recovery) (Table 3).

Table 3. Hexazinone recovery in fresh and air-dried samples from spiked (0.5 kg/ha) humus soils

| Replication | Hexazinone Residues | | | | | |
|---|---|---|---|---|---|---|
| | Wet Soil | | | Air-Dried Soil | | |
| Format | µg/g | µg/mL | kg/ha | µg/g | µg/mL | kg/ha |
| 1 | 1.03 | 0.93 | 0.46 | 2.54 | 1.11 | 0.56 |
| 2 | 1.11 | 0.99 | 0.50 | 2.58 | 1.13 | 0.57 |
| 3 | 1.06 | 0.95 | 0.47 | 2.45 | 1.07 | 0.54 |
| 4 | 1.90 | 1.70 | 0.85 | 2.38 | 1.05 | 0.52 |
| Mean | 1.28 | 1.14 | 0.57 | 2.49 | 1.09 | 0.55 |
| CV | 33% | 33% | 33% | 4% | 4% | 4% |
| Recovery | | | 114% | | | 110% |

The overall consistency of procedures used for subsampling, residue extraction, cleanup, and analysis by gas chromatography was examined. Fifty replicated subsamples from a homogenized air-dried mineral soil were individually processed and analyzed. Results indicated high reproducibility, with a mean hexazinone residue concentration of 0.84% µg/g, 6.9% CV and a range of 0.66 - 0.95 µg/g. The modifications made to Holt's (1981) procedures for extraction and analysis improved both simplicity and reproducibility.

*Hexazinone Residue Persistence and Leaching in Soils*

Hexazinone residues measured in soils at 0-time (1.99 kg/ha) were 79% of that indicated by on-target deposition collector plates (2.53 kg/ha) and 52% of the planned application rate. The unexpectedly low residue values in the soil were probably from residue loss during handling or shipping. Recovery trials described above indicated that thoroughly blended fresh humus soils at 56% moisture content could be handled and stored with no residue loss. However, the concentrated nature of residues in a thin surface layer containing all or most of the residue applied may be the cause of the apparent residue loss when the sample comes into contact with the inner wall of the sample bags. The vulnerability of these high residue concentrations in the surface layer would probably persist until rainfall initiated leaching into lower layers. In this study, rainfall occurred prior to the soil collection on day 6, but samples from day 3 (2 mm cumulative rainfall) may have incurred similar losses as those from 0-time. To avoid potential residue losses through contact with sample bags in future 0-time samples, the following procedure is recommended:

1) Half-fill a set of glass jars (5 cm deep and 10 cm diameter) with pre-spray soils obtained from the field.

2) Submerge the jars to the ground level and expose them to herbicide application at the soil plots.

3) Re-fill the jars to the top with pre-spray soils and seal the jar with a glass cover.

4) Weigh the whole sample and calculate the bulk density to enable the residues analyzed in µ g/g to be converted to kg/ha to directly compare with the deposition or application rates.

Average hexazinone residues in the combined upper and lower layers (0-30 cm) increased from 1.87 kg/ha, 3 days after application, to a peak of 2.04 kg/ha, 6 days after application, when rainfall had accumulated from 2 to 29 mm. Residues then disappeared rapidly to averages of 0.94, 1.05, 0.27, 0.27, 0.22, 0.11 and 0.09 kg/ha at 13, 31, 61, 87, 122, 157 and 361 days after application, respectively, with cumulative rainfall at 113, 172, 344, 419, 465, 539 mm and snow (Fig. 2). No residues were detected 453 and 537 days after application. Metabolite A was found at low levels, less than 0.26 kg/ha, in 5 out of 48 soil cores between 3 and 31 days after application. Metabolite B, the only major metabolite that shows phytotoxicity (Sung 1985), was found at less than 0.15 kg/ha in 10 out of 48 soil cores between 6 and 122 days after application.

The rate of hexazinone dissipation is estimated by a linear regression of two variables, the hexazinone residues (kg/ha) (Wa) and days after application (D), and expressed as: $\log Wa = a + b \log D$ (Table 4). Data collected between 3 and 361 days after application were used to obtain the intercept (a = 0.78) and the slope (b = -0.711) (Table 4). Results of the F-test for the linear regression were significant (P = 0.01). The coefficient of linear regression determination ($r^2$) indicated that the regression equation accounted for 91% of the variation in the data. The signifi-

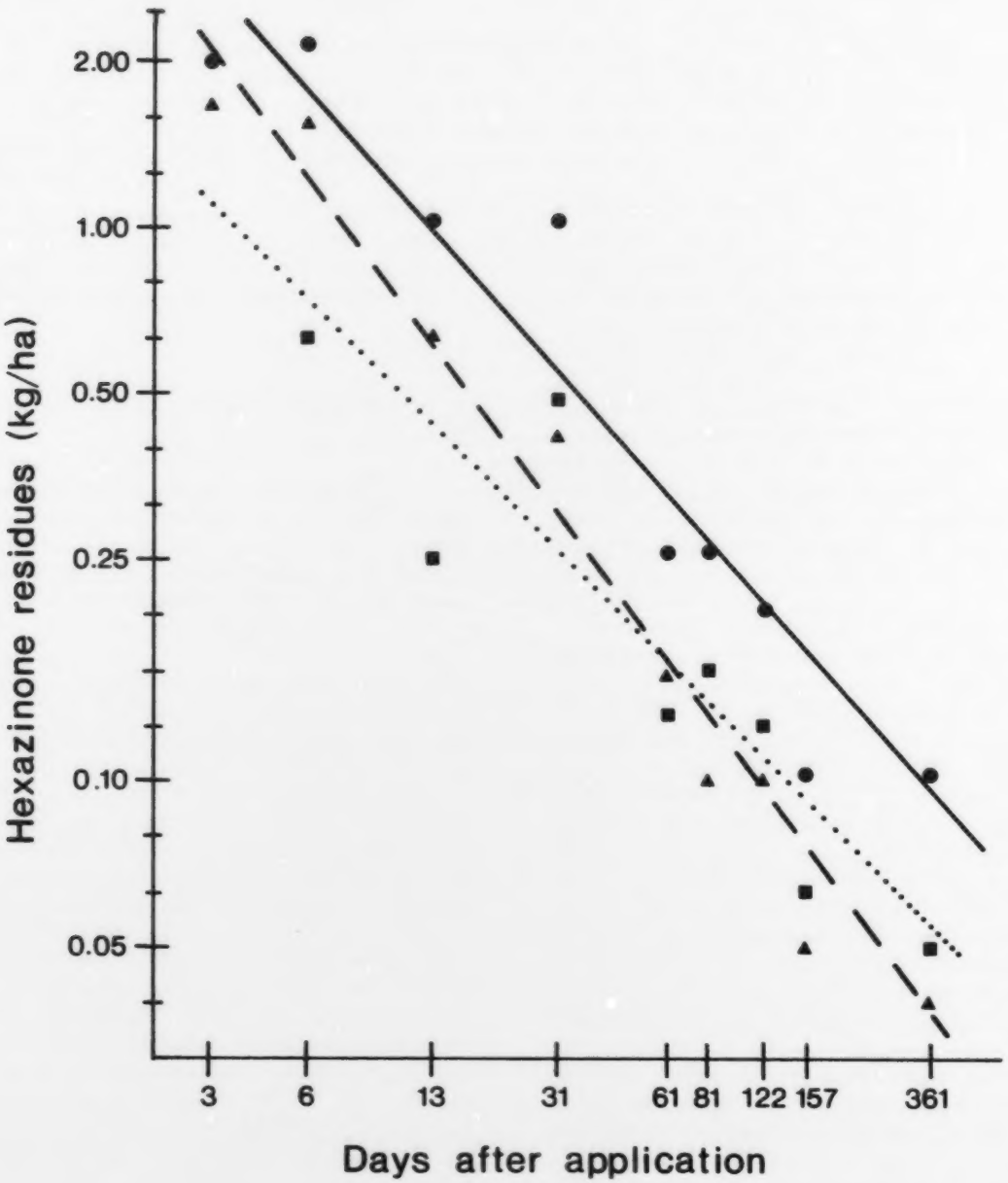


Figure 2. Dissipation of hexazinone at different depths in New Brunswick loam soils treated on 19 May 1984; ●, total soil core (0-30 cm); ▲, upper layer (0-15 cm); ■, lower layer (15-30 cm); and their "best fit" regression lines: —— (0-30cm), --- (0-15 cm), .... (15-30 cm).

Table 4. Equations illustrating temporal dissipation of hexazinone in New Brunswick loam soils at different depths

| Soil Layer | Soil Depth (cm) | Linear Regression Equation[a] | Correlation Coefficient | N |
|---|---|---|---|---|
| Total | 0-30 | log Wa = 0.781 - 0.711 log D | 0.953 | 9 |
| Upper | 0-15 | log Wa = 0.803 - 0.891 log D | 0.980 | 9 |
| Lower | 15-30 | log Wa = 0.288 - 0.605 log D | 0.879 | 9 |
| Upper | 0-15 | log Ww = 0.743 - 0.887 log D | 0.975 | 9 |
| Lower | 15-30 | log Ww = 0.130 - 0.563 log D | 0.876 | 9 |

[a] Wa = Hexazinone residues on area basis (kg/ha); D = days after application; Ww = Hexazinone residues on weight basis (μg/g).

cant correlation coefficient (r) indicated that data values fitted very closely to regression line (r = 0.953). Dissipation times (DT) required for 50% ($DT_{50}$) and 90% ($DT_{90}$) disappearance of hexazinone were estimated from the linear regression and were 13 and 122 days, respectively.

Dissipation of hexazinone in the upper soil layer (0-15 cm) was faster than in the combined total soil core (0-30 cm). Hexazinone residues were 1.87, 1.44, 0.67, 0.52, 0.14, 0.10, 0.99, 0.05 and 0.04 kg/ha after 3, 13, 31, 61, 87, 122, 157 and 361 days, respectively (Fig. 2). No residues were found 453 and 537 days after application. The $DT_{50}$ and $DT_{90}$ values in this soil layer were 8 and 49 days, respectively. The shorter DT values indicated leaching of hexazinone into the lower soil layer (15-30 cm), which was first observed 6 days after application at 0.60 kg/ha (peak value) when rainfall had accumulated to 29 mm. Dissipation rate in this soil layer was much slower ($DT_{50}$ = 28 days; $DT_{90}$ = 319 days) than in the upper layer and in the combined total soil core. The measured hexazinone residues were 0.60, 0.27, 0.53, 0.13, 0.17, 0.13, 0.06 and .05 kg/ha after 6, 13, 31, 61, 87, 122, 157 and 361 days (Fig. 2). No residues were found 453 and 537 days after application. Significant linear regressions and correlation coefficients (P = 0.01) for both upper and lower soil layers are reported in Table 4.

Results of this study did not preclude the possibility of hexazinone being leached into soils deeper than 30 cm. However, actual data suggested that in New Brunswick loam soil, hexazinone did not persist after 1 year or one growing season.

Hexazinone concentration measured on weight basis (μg/g) (Table 5) showed similar regression and correlation (Table 4) as that on area basis (kg/ha). The similarity of soil chemical properties and textures among soil plots and between the upper and lower layers (Table 6) masked the improvement in r and $r^2$ values for residue disappearance relationships generally offered by the kg/ha format. Only about 15% of the soil cores from the upper 15 cm layer contained an organic layer separable from mineral horizons. Bulk densities of soil samples containing organic layers may be highly variable. Differences in format results, with kg/ha showing greater consistency and therefore higher r and $r^2$ values, would be more pronounced if a variable organic layer is prevalent. High spatial variability of residues in field soils found in other studies may be from both extrinsic and intrinsic sources (Rao and Wagenet 1985).

Table 5. Averaged concentration of hexazinone residues (N = 4) on weight basis (μg/g) in New Brunswick loam soils

| Days After[a] Application | Upper Soil Layer (0-15 cm) | Lower Soil Layer (15-30 cm) | Cumulative Rainfall (mm) |
|---|---|---|---|
| 0 | 1.65 + 0.40 | 0.03[b] | 0 |
| 3 | 1.46 + 0.59 | 0.03 | 2 |
| 6 | 1.30 + 0.21 | 0.46 + 0.31 | 29 |
| 13 | 0.58 + 0.06 | 0.23 + 0.17 | 113 |
| 31 | 0.52 + 0.36 | 0.44 + 0.32 | 172 |
| 61 | 0.12 + 0.09 | 0.09 + 0.10 | 344 |
| 87 | 0.11 + 0.09 | 0.12 + 0.09 | 419 |
| 122 | 0.07 + 0.04 | 0.10 + 0.06 | 465 |
| 157 | 0.05 + 0.10 | 0.06 + 0.04 | 539 |
| 361 | 0.03 + 0.04 | 0.05 + 0.05 | Snow |
| 453 | 0.03 | 0.03 | |
| 537 | 0.03 | 0.03 | |

[a] 0-time on 19 May 1984
[b] Limit of Detection = 0.03 μg/g

Table 6. Chemical properties and texture of New Brunswick loam soils

| Layer | Upper (0 - 15 cm) Mean | SD | Lower (15 - 30 cm) Mean | SD | Total (0 - 31 cm) Mean | SD |
|---|---|---|---|---|---|---|
| %N | 0.126 | 0.023 | 0.142 | 0.080 | 0.135 | 0.059 |
| %P | 0.0012 | 0.0003 | 0.0022 | 0.0012 | 0.0018 | 0.0010 |
| %K | 0.0093 | 0.0040 | 0.0059 | 0.0032 | 0.0074 | 0.0037 |
| pH | 5.13 | | 5.06 | | 5.09 | |
| CEC (meq/100g) | 16.558 | 2.533 | 17.001 | 6.639 | 16.811 | 4.923 |
| %OM | 3.194 | 0.794 | 4.228 | 2.724 | 3.785 | 2.056 |
| %Sand | 47.4 | 1.8 | 48.2 | 2.6 | 47.9 | 2.2 |
| %Silt | 33.0 | 2.0 | 32.2 | 3.9 | 32.5 | 3.0 |
| %Clay | 19.6 | 2.1 | 19.6 | 2.2 | 19.6 | 2.0 |
| Number of replicates | 4 | | 4 | | 8 | |

The moisture content of soils varied little during the 537 day sample schedule. The mean moisture content of the upper layer (27.2% ± 5.9) was very comparable to that of the lower layer (27.9% ± 5.2). A minor peak in moisture content in the upper layer was found on the 6th day after application after the first rainfall. Lower layer samples from the 6th day also contained the highest residue concentrations (0.6 kg/ha), indicating residue leaching during the first rainfall. Station No. 2 showed the greatest leaching from the upper layer (1.06 kg/ha) to the lower layer (1.16 kg/ha) on the 6th day and also had the highest moisture content (41.7%) and no separable organic layer. These results related hexazinone residue leaching directly to the initial rainfall and to soil porosity, which restricts or inhibits the flow of soil water.

*Lateral residue Movement Downslope*

The 0-time residue concentrations in soil samples collected at distances off-target down a 5% slope reflected the rate of off-target drift from the aerial application. The extinction rates were similar but values were lower in soil samples (0.47, 0.13 and 0.03 kg/ha) than from deposition collectors (0.85, 0.31 and 0.050 kg/ha at 10, 20 and 50 m downwind, respectively) (Table 2, 7). The lower soil residue values may be from residue loss through the sample bags. A significant ($p < 0.05$) log-log extinction rate relationship ($\log Y = 1.36 - 1.70 \log X$) was found for 0-time where Y = residue in soils (kg/ha) and X = distance (m) downwind, with $r = 0.999$ and $r^2 = 0.998$.

Increased residue concentrations at off-target sites after the initial rainfall indicated some lateral hexazinone movement. The stations at 10 and 20 m down a 5% slope showed lateral hexazinone movement from 6 to 61 days after application (Table 7). Lateral hexazinone movement at 50 m downslope was found in trace amounts near the detection limit in the first two weeks. No residues were detected in soil samples from 100 m downslope at any time in the sample schedule. Downslope hexazinone residue movement was also observed in other studies (Harrington et al. 1982; Barring and Torstensson 1983). Vertical hexazinone leaching from the upper to lower soil layers also occurred in the off-target stations (Table 7). This vertical leaching suggests that soil samples collected only from surface layers may be insufficient to appropriately quantify residue runoff down a slope. Hexazinone metabolites A and B were not detected in any of the off-target samples. The limits of detection were 0.03, 0.10 and 0.06 µg/g for hexazinone, metabolite A and B, respectively.

*Off-Site Residue Movement in Stormflow and Baseflow (Snowmelt)*

Six storm events were monitored for hexazinone residue in streamwater between 25 May and 3 July 1984. Hexazinone residues were found throughout the 45 day period and during each storm event (Table 8). Residues decreased to about 10% in samples collected at the station 50 m downstream from 30.8 ppb in the first storm event to 3.7 ppb in the 6th storm event. These findings were in agreement with those reported by Neary et al. (1983; 1986), that residues in runoff peaked in the first storm after application. No metabolite A or B residues were detected in any of the water samples in this study. A lag time was indicated by the absence of detectable hexazinone (i.e., < 0.5 ppb) in samples collected 800 m downstream during the first storm event and first day of the second storm event (Table 8). The magnitude of the second storm event (the largest with 84 mm rainfall) was probably required to generate sufficient flow to transport residues longer distances in the otherwise slowly flowing ephemeral stream. The flow in all six storm events was insufficient to transport hexazinone residue in detectable quantities to the station 1500 m downstream (Table 8). The The duration of lateral residue movement in soils discussed above (6-61 days) roughly coincides with the period that samples were collected (and residues detected) in storm runoff.

The accuracy of analysis of hexazinone in water samples was demonstrated with the results of a spike-recovery trial. The recovery of 5 and 50 ppb hexazinone in water (N = 4) was 100.4 ± 7.6% and 99.2 ± 8.4%, respectively.

Table 7. Lateral hexazinone movement (kg/ha) down a 5% slope

| Days[a] Postspray | Soil[b] Layer | Off-Site and Downslope Distance | | | | Cumulative Rainfall (mm) |
|---|---|---|---|---|---|---|
| | | 10 m | 20 m | 50 m | 100 m | |
| 0 | U | 0.47 | 0.13 | 0.03 | ND | 0 |
| | L | ND | ND | ND | ND | |
| | T | 0.47 | 0.13 | 0.03 | ND | |
| 6 | U | 0.74 | 0.20 | 0.05 | ND | 29 |
| | L | 0.31 | 0.07 | ND | ND | |
| | T | 1.05 | 0.27 | 0.05 | ND | |
| 13 | U | 0.49 | 0.21 | 0.11 | ND | 113 |
| | L | 0.21 | 0.34 | ND | ND | |
| | T | 0.70 | 0.55 | 0.11 | ND | |
| 31 | U | 0.66 | 0.21 | 0.04 | ND | 172 |
| | L | 0.36 | 0.22 | ND | ND | |
| | T | 1.02 | 0.43 | 0.04 | ND | |
| 61 | U | 0.38 | 0.06 | 0.02 | ND | 344 |
| | L | ND | 0.12 | ND | ND | |
| | T | 0.38 | 0.18 | 0.02 | ND | |
| 87 | U | 0.09 | 0.05 | ND | ND | 419 |
| | L | 0.12 | 0.14 | ND | ND | |
| | T | 0.21 | 0.19 | ND | ND | |
| 122 | U | 0.03 | ND | ND | ND | 465 |
| | L | 0.07 | ND | ND | ND | |
| | T | 0.10 | ND | ND | ND | |
| 157 | U | 0.05 | ND | ND | ND | 539 |
| | L | ND | ND | ND | ND | |
| | T | 0.05 | ND | ND | ND | |
| 361 | U | 0.05 | 0.07 | ND | ND | Snow |
| | L | ND | ND | ND | ND | |
| | T | 0.05 | 0.07 | ND | ND | |
| 453 | U | ND | 0.04 | ND | ND | |
| | L | ND | ND | ND | ND | |
| | T | ND | 0.04 | ND | ND | |
| 537 | U | ND | ND | ND | ND | |
| | L | ND | ND | ND | ND | |
| | T | ND | ND | ND | ND | |

[a] 0-time on 19 May 1984.

[b] U = Upper (0-15 cm); L = Lower (15-30 cm); T = Total (0-30 cm).
ND = Not Detectable; Limit of Detection about 0.02 kg/ha.

Table 8. Sample collection times during storm events and hexazinone residue concentration in streamwater at three downstream distances

| Days[a] Postspray | Storm Event No. | Days Poststorm | Cumulative Rainfall (mm) | Hexazinone (ppb) 50 m | 800 m | 1500 m |
|---|---|---|---|---|---|---|
| 6 | 1 | | 29 | 30.8 | ND | ND |
| 8 | | 2 | 29 | 17.9 | ND | ND |
| 11 | 2 | | 74 | 13.4 | ND | ND |
| 13 | | 2 | 113 | 19.1 | 5.1 | ND |
| 16 | | 3 | 116 | 10.4 | 3.1 | ND |
| 20 | | 7 | 116 | 6.5 | 0.9 | ND |
| 27 | 3 | | 134 | 7.7 | 0.7 | ND |
| 31 | 4 | | 172 | 7.1 | 0.8 | ND |
| 34 | | 3 | 175 | 5.7 | 0.8 | ND |
| 38 | 5 | | 201 | 3.9 | 0.7 | ND |
| 45 | 6 | | 236 | 3.7 | 1.0 | ND |

[a]0-time at 19 May 1984.
ND = Not Detectable; Limit of detection was 0.5 ppb.

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Appendix 1. Hexazinone residue persistence and leaching data (kg/ha)

| Days[a] Postspray | Soil[b] Layer | Station Number 1 | 2 | 3 | 4 | Mean | SD |
|---|---|---|---|---|---|---|---|
| 0 | U | 2.10 | 1.74 | 2.11 | 2.03 | 1.99 | 0.19 |
| | L | ND | ND | ND | ND | ND | |
| | T | 2.10 | 1.71 | 2.11 | 2.03 | 1.99 | 0.19 |
| 3 | U | 2.07 | 1.01 | 1.49 | 2.89 | 1.87 | 0.81 |
| | L | ND | ND | ND | ND | ND | |
| | T | 2.07 | 1.01 | 1.49 | 2.89 | 1.87 | 0.81 |
| 6 | U | 1.69 | 1.06 | 1.94 | 1.08 | 1.44 | 0.44 |
| | L | 0.57 | 1.16 | 0.53 | 0.13 | 0.60 | 0.42 |
| | T | 2.26 | 2.22 | 2.47 | 1.21 | 2.04 | 0.56 |
| 13 | U | 0.83 | 0.64 | 0.53 | 0.66 | 0.67 | 0.12 |
| | L | 0.20 | 0.52 | 0.30 | 0.05 | 0.27 | 0.20 |
| | T | 1.03 | 1.16 | 0.83 | 0.71 | 0.93 | 0.20 |
| 31 | U | 0.18 | 0.52 | 0.86 | 0.53 | 0.52 | 0.28 |
| | L | 0.28 | 0.13 | 0.87 | 0.84 | 0.53 | 0.38 |
| | T | 0.46 | 0.65 | 1.73 | 1.37 | 1.05 | 0.60 |
| 61 | U | 0.05 | 0.18 | 0.27 | 0.06 | 0.14 | 0.10 |
| | L | 0.11 | ND | 0.08 | 0.32 | 0.13 | 0.14 |
| | T | 0.16 | 0.18 | 0.35 | 0.38 | 0.27 | 0.11 |
| 87 | U | 0.09 | 0.11 | 0.06 | 0.15 | 0.10 | 0.04 |
| | L | 0.17 | ND | 0.26 | 0.23 | 0.17 | 0.12 |
| | T | 0.26 | 0.11 | 0.32 | 0.38 | 0.27 | 0.12 |
| 122 | U | 0.20 | 0.09 | 0.05 | 0.03 | 0.09 | 0.08 |
| | L | 0.22 | 0.09 | 0.12 | 0.10 | 0.13 | 0.06 |
| | T | 0.42 | 0.18 | 0.17 | 0.13 | 0.23 | 0.13 |
| 157 | U | ND | 0.21 | ND | ND | 0.05 | 0.11 |
| | L | 0.06 | 0.03 | 0.05 | 0.10 | 0.06 | 0.03 |
| | T | 0.06 | 0.24 | 0.05 | 0.10 | 0.11 | 0.09 |
| 361 | U | ND | 0.08 | ND | 0.06 | 0.04 | 0.04 |
| | L | 0.11 | ND | ND | 0.10 | 0.05 | 0.06 |
| | T | 0.11 | 0.08 | ND | 0.16 | 0.09 | 0.07 |
| 453 | U | ND | ND | ND | ND | ND | |
| | L | ND | ND | ND | ND | ND | |
| | T | ND | ND | ND | ND | ND | |

[a] 0-time on 19 May 1984.
[b] U = Upper (0-15 cm); L = Lower (15-30 cm); T = Total (0-30 cm).
ND = Not Detectable; Limit of Detection about 0.02 kg/ha.

Appendix 2. Hexazinone residue persistence and leaching data (μg/g)

| Days[a] Postspray | Soil[b] Layer | Station Number 1 | 2 | 3 | 4 | Mean | SD |
|---|---|---|---|---|---|---|---|
| 0 | U | 1.44 | 1.35 | 1.57 | 2.23 | 1.65 | 0.40 |
| | L | ND | ND | ND | ND | ND | |
| | T | 1.44 | 1.35 | 1.57 | 2.23 | 1.65 | 0.40 |
| 3 | U | 1.55 | 0.76 | 1.33 | 2.19 | 1.46 | 0.59 |
| | L | ND | ND | ND | ND | ND | |
| | T | 1.55 | 0.76 | 1.33 | 2.19 | 1.46 | 0.59 |
| 6 | U | 1.30 | 1.40 | 1.49 | 1.00 | 1.30 | 0.21 |
| | L | 0.49 | 0.87 | 0.35 | 0.13 | 0.46 | 0.31 |
| | T | 1.79 | 2.27 | 1.84 | 1.13 | 1.76 | 0.47 |
| 13 | U | 0.61 | 0.54 | 0.65 | 0.52 | 0.58 | 0.06 |
| | L | 0.15 | 0.31 | 0.42 | 0.04 | 0.23 | 0.17 |
| | T | 0.76 | 0.85 | 1.07 | 0.56 | 0.81 | 0.21 |
| 31 | U | 0.14 | 0.43 | 0.51 | 1.01 | 0.52 | 0.36 |
| | L | 0.30 | 0.08 | 0.53 | 0.83 | 0.44 | 0.32 |
| | T | 0.44 | 0.51 | 1.04 | 1.84 | 0.96 | 0.65 |
| 61 | U | 0.03 | 0.14 | 0.24 | 0.06 | 0.12 | 0.09 |
| | L | 0.07 | ND | 0.05 | 0.23 | 0.09 | 0.10 |
| | T | 0.10 | 0.14 | 0.29 | 0.29 | 0.21 | 0.10 |
| 87 | U | 0.09 | 0.08 | 0.04 | 0.24 | 0.11 | 0.09 |
| | L | 0.11 | ND | 0.15 | 0.22 | 0.12 | 0.09 |
| | T | 0.20 | 0.08 | 0.19 | 0.46 | 0.23 | 0.16 |
| 122 | U | 0.12 | 0.07 | 0.05 | 0.03 | 0.07 | 0.04 |
| | L | 0.18 | 0.05 | 0.07 | 0.09 | 0.10 | 0.06 |
| | T | 0.30 | 0.12 | 0.12 | 0.12 | 0.17 | 0.09 |
| 157 | U | ND | 0.19 | ND | ND | 0.05 | 0.10 |
| | L | 0.05 | 0.03 | 0.03 | 0.12 | 0.06 | 0.04 |
| | T | 0.05 | 0.22 | 0.02 | 0.12 | 0.11 | 0.09 |
| 361 | U | ND | 0.08 | ND | 0.05 | 0.03 | 0.04 |
| | L | 0.09 | ND | ND | 0.09 | 0.05 | 0.05 |
| | T | 0.09 | 0.08 | ND | 0.14 | 0.08 | 0.06 |
| 453 | U | ND | ND | ND | ND | ND | |
| | L | ND | ND | ND | ND | ND | |
| | T | ND | ND | ND | ND | ND | |
| 537 | U | ND | ND | ND | ND | ND | |
| | L | ND | ND | ND | ND | ND | |
| | T | ND | ND | ND | ND | ND | |

[a]0-time on 19 May 1984.
[b]U = Upper (0-15 cm); L = Lower (15-30 cm); T = Total (0-30 cm).
ND = Not Detectable; Limit of Detection 0.03 μg/g.

Appendix 3. Appearance of metabolites A and B after hexazinone treatment in New Brunswick loam soils

| Days[a] Post-Spray | Soil[b] Layer | Metabolite A | | Metabolite B | | Cumulative Rainfall (mm) |
|---|---|---|---|---|---|---|
| | | kg/ha | µg/g | kg/ha | µg/g | |
| 0 | U | ND | ND | ND | ND | 0 |
| | L | ND | ND | ND | ND | |
| 3 | U | (0.26)[c] | (0.20) | ND | ND | 2 |
| | L | ND | ND | ND | ND | |
| 6 | U | 0.09±0.01 | 0.08±0.01 | (0.09,0.08) | (0.07,0.06) | 29 |
| | L | ND | ND | ND | ND | |
| 13 | U | (0.09) | (0.07) | (0.08) | (0.06) | 113 |
| | L | ND | ND | ND | ND | |
| 31 | U | (0.15,0.05) | (0.12,0.09) | (0.12,0.06) | (0.07,0.12) | 172 |
| | L | (0.16,0.08) | (0.10,0.08) | (0.15,0.09) | (0.09,0.09) | |
| 61 | U | ND | ND | ND | ND | 344 |
| | L | ND | ND | (0.08) | (0.06) | |
| 87 | U | ND | ND | (0.06) | (0.06) | 419 |
| | L | ND | ND | (0.11,0.09) | (0.7,0.08) | |
| 122 | U | ND | ND | (0.13) | (0.08) | 465 |
| | L | ND | ND | (0.09) | (0.07) | |
| 157 | U | ND | ND | ND | ND | 539 |
| | L | ND | ND | ND | ND | |
| 361 | U | ND | ND | ND | ND | Snow |
| | L | ND | ND | ND | ND | |
| 453 | U | ND | ND | ND | ND | |
| | L | ND | ND | ND | ND | |
| 537 | U | ND | ND | ND | ND | |
| | L | ND | ND | ND | ND | |

[a] 0-time on 19 May 1984.

[b] U = Upper (0-15 cm); L = Lower (15-30 cm).

[c] Values in () indicate less than four detectable values, otherwise n=4.

ND = Not Detectable; Limit of Detection = 0.03, 0.10 and 0.06 µg/g for hexazinone, metabolite A and B, respectively, and about 0.02 kg/ha for hexazinone.

Appendix 4. Soil bulk density data from the residue persistence sites Station No. Upper Layer (0-15 cm) Station No. Lower Layer (15-30 cm)

| Days[a] Postspray | Station No. Upper Layer (0-15 cm) | | | | Station No. Lower Layer (15-30 cm) | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | t 4 |
| 0 | 0.973 | 0.843 | 0.895 | 0.606 | 1.226 | 1.032 | 0.601 | 0.841 |
| 3 | 0.889 | 0.891 | 0.749 | 0.878 | 1.001 | 1.038 | 0.747 | 1.009 |
| 6 | 0.863 | 0.505 | 0.869 | 0.722 | 0.766 | 0.885 | 0.994 | 0.689 |
| 13 | 0.904 | 0.799 | 0.538 | 0.836 | 0.904 | 1.114 | 0.466 | 0.789 |
| 31 | 0.840 | 0.821 | 1.126 | 0.351 | 0.614 | 1.102 | 1.083 | 0.679 |
| 61 | 0.951 | 0.882 | 0.765 | 0.770 | 1.074 | 1.441 | 1.031 | 0.912 |
| 87 | 0.650 | 0.954 | 0.958 | 0.412 | 1.005 | 1.186 | 1.148 | 0.723 |
| 122 | 1.076 | 0.815 | 0.702 | 0.608 | 0.836 | 1.117 | 1.082 | 0.782 |
| 157 | 0.938 | 0.759 | 0.768 | 0.610 | 0.882 | 0.771 | 1.008 | 0.557 |
| 361 | 1.094 | 0.678 | 0.938 | 0.829 | 0.880 | 0.665 | 1.039 | 0.852 |
| 453 | 0.862 | 0.796 | 1.039 | 0.727 | 0.877 | 1.070 | 1.088 | 0.854 |
| 537 | 1.073 | 0.665 | 1.145 | 0.632 | 1.453 | 1.020 | 1.167 | 1.061 |
| Mean | 0.926 | 0.784 | 0.874 | 0.665 | 0.959 | 1.04 | 0.955 | 0.812 |
| SD | 0.124 | 0.121 | 0.180 | 0.163 | 0.219 | 0.199 | 0.225 | 0.142 |
| N | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |
| Total | Mean = 0.812 | | N = 48 | | Mean = 0.942 | | N = 48 | |

[a] 0-time on 19 May 1984.

Appendix 5. Soil moisture content data from the residue persistence

| Days[a] Postspray | Soil[b] Layer | Station Number 1 | 2 | 3 | 4 | Mean | SD |
|---|---|---|---|---|---|---|---|
| 0 | U | 25.4 | 31.8 | 27.7 | 30.5 | 28.9 | 2.9 |
| | L | 24.5 | 27.4 | 32.8 | 26.3 | 27.8 | 3.6 |
| 3 | U | 24.1 | 26.8 | 25.5 | 25.9 | 25.6 | 1.1 |
| | L | 26.7 | 22.5 | 34.1 | 20.0 | 25.8 | 6.2 |
| 6 | U | 23.4 | 41.7 | 33.4 | 28.1 | 31.7 | 7.8 |
| | L | 28.0 | 32.5 | 27.2 | 31.2 | 29.7 | 2.5 |
| 13 | U | 27.0 | 24.8 | 30.6 | 22.6 | 26.3 | 3.4 |
| | L | 30.4 | 24.4 | 42.0 | 37.4 | 33.6 | 7.7 |
| 31 | U | 21.4 | 35.1 | 26.4 | 36.3 | 29.8 | 7.1 |
| | L | 32.8 | 24.6 | 29.0 | 41.7 | 32.0 | 7.3 |
| 61 | U | 25.1 | 30.3 | 30.1 | 19.6 | 26.3 | 5.1 |
| | L | 26.7 | 16.6 | 29.6 | 29.3 | 25.6 | 6.1 |
| 87 | U | 27.6 | 28.7 | 23.2 | 37.6 | 29.3 | 6.0 |
| | L | 26.1 | 21.7 | 25.2 | 33.4 | 26.6 | 4.9 |
| 122 | U | 16.7 | 32.1 | 19.5 | 8.9 | 19.3 | 9.6 |
| | L | 22.8 | 23.4 | 21.3 | 22.5 | 22.5 | 8.8 |
| 157 | U | 21.6 | 34.5 | 25.9 | 24.9 | 26.7 | 5.5 |
| | L | 27.3 | 33.6 | 27.6 | 29.1 | 29.4 | 2.9 |
| 361 | U | 22.0 | 35.0 | 29.2 | 26.9 | 28.3 | 5.4 |
| | L | 31.5 | 34.9 | 26.7 | 28.8 | 30.5 | 3.5 |
| 453 | U | 19.9 | 30.7 | 23.2 | 28.3 | 25.5 | 4.9 |
| | L | 22.5 | 26.6 | 25.9 | 29.9 | 26.6 | 3.0 |
| 537 | U | 29.7 | 35.5 | 22.2 | 28.9 | 29.1 | 5.4 |
| | L | 20.8 | 27.0 | 25.4 | 27.9 | 25.3 | 3.2 |
| Total | U | (n=48) | | | | 27.2 | 5.9 |
| | L | (n=48) | | | | 27.9 | 5.2 |

[a] 0-time on 19 May 1984.
[b] U = Upper (0-15 cm); L = Lower (15-30 cm).